

A MODERN APPROACH TO ORGANIC CHEMISTRY

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EDICION REVOLUCIONARIA



LA HABANA, 1968

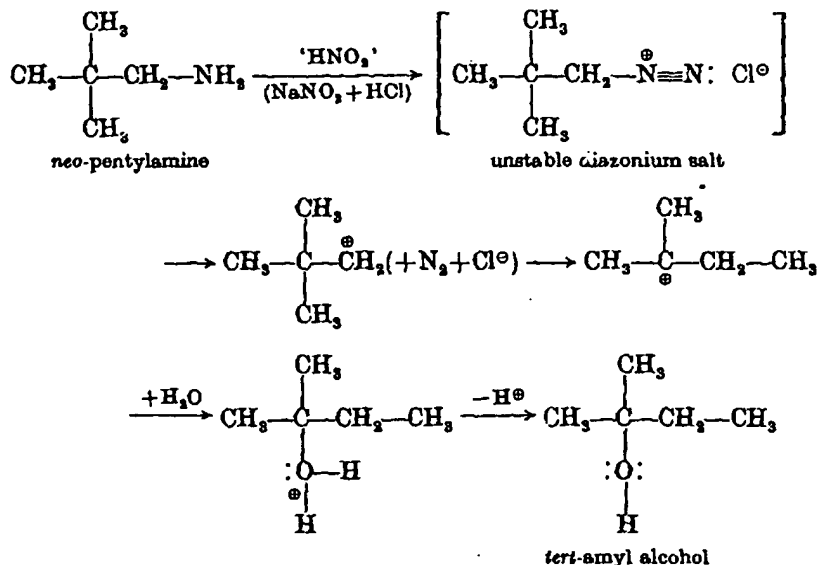
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THIOETHERS

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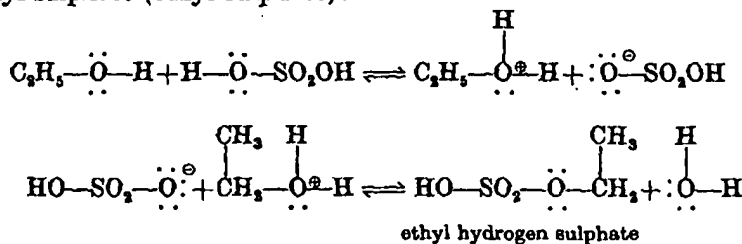
reactions of *neo*-
nary reactions of
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chol (*S_N2* mechan-
then treated with
reaction at a much
l halides), yielding

ALCOHOLS, ETHERS, THIOALCOHOLS, AND THIOETHERS 175



Amylenes, formed by an elimination reaction from the *tert*-amyl cation, are frequently co-products in these reactions. Rearrangements of *neo*-pentyl to *tert*-amyl derivatives are commonly known as WHITMORE REARRANGEMENTS.†

When alcohols are treated with sulphuric acid, several different reactions occur depending on the temperature and the relative proportions in which the alcohol and acid are taken. Warmed to about 80° C ethyl alcohol and sulphuric acid give ethyl hydrogen sulphate and some diethyl sulphate (ethyl sulphate):

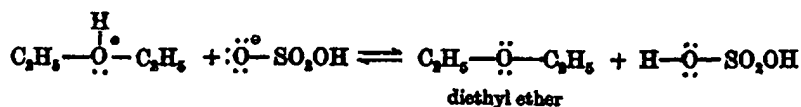
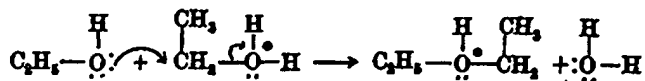
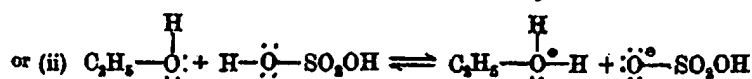
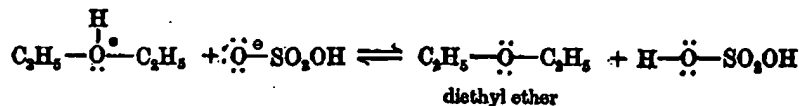
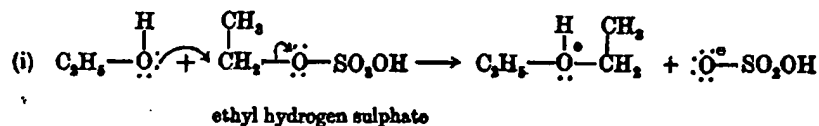


A similar further reaction between ethyl hydrogen sulphate and alcohol leads to the diethyl sulphate. Dimethyl and diethyl sulphates are best prepared by the reaction of disulphuric acid, chlorosulphonic acid, or sulphuryl chloride on the corresponding alcohol. In general, when the alcohol is heated to higher temperatures with sulphuric acid,

† Rearrangements having a similar mechanism occur with several other classes of compounds. These are often referred to collectively as WAGNER-TYPE rearrangements.

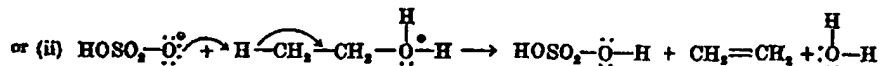
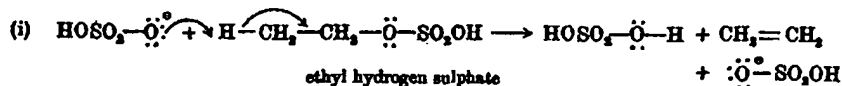
two other reactions occur, as illustrated for the case of ethyl alcohol:

(a) SUBSTITUTION. Two mechanisms are possible, either



Mechanism (ii) does not represent the alkyl hydrogen sulphate as a necessary intermediate and is given support by the fact that ethyl alcohol yields ether when heated with hydrogen chloride in a closed vessel at 150°–160° C, under which conditions ethyl chloride (the intermediate corresponding to ethyl hydrogen sulphate in (i) above) and ethyl alcohol do not react (van Alphen, 1930). The evidence, however, is insufficient for a definite mechanism to be assigned; it is not unlikely that both mechanisms operate. There is also insufficient direct experimental evidence on which to decide whether a carbonium ion is produced as an intermediate, i.e. whether the mechanism is unimolecular (S_N1) or bimolecular (S_N2).

(b) ELIMINATION. Again two mechanisms can be formulated, either



Here also mechanism (ii) does not represent the alkyl hydrogen sulphate as an intermediate but a decision between (i) and (ii) must await further evidence; again it is conceivable that both mechanisms may operate.

An excess of the alcohol is necessary for the substitution reaction and ether production. Excess of acid and high temperatures favour elimination and hence olefin formation. Tertiary alcohols yield olefins and not